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The sacrificial removal, or ablation, of a composite material undergoing internal chemical degradation to accommodate the high rates of surface heating experienced by vehicles during planetary entry may be characterized mathematically by the following governing partial differential equation for temperature

$$\rho c_{p} \frac{dT}{d\theta} = \frac{\partial}{\partial x} \left[k \frac{\partial T}{\partial x} \right] + \dot{m}_{g} \frac{\partial Hg}{\partial x} + \frac{\partial \rho}{\partial \theta} H_{d}$$
 (1)

where the heat accumulation term on the left is balanced respectively by conduction, flow of chemical energy and decomposition energy. Although the equation has been simplified somewhat by considering a one-dimensional situation, the coefficients are all temperature dependent. The associated boundary conditions are the conservation of energy at the receding surface:

Imposed Coupling of Ablator Re-
Heating sponse with Imposed Heating
$$\dot{q}_r + \dot{q}_c - \{\dot{q}_{rr} + \dot{q}_B - \dot{q}_{chem}\} = k \frac{\partial T}{\partial x}$$
(2)

and the instantaneous position of the surface:

$$x_{o}(0) - x_{o}(t) = \int_{0}^{t} \dot{x}_{o} dt$$
 (3)

The mathematical formulation is completed by specifying the condition at the rear surface of the material, i.e., for an insulated surface

$$k \left. \frac{\partial T}{\partial x} \right|_{L} = 0 \tag{4}$$

Since the reradiated term \dot{q}_{rr} in equation (2) is proportional to the fourth power of temperature, we have a highly nonlinear boundary condition. Furthermore the blockage and chemical terms $\,\,\dot{q}_{B}^{}$ and $\dot{q}_{chem}^{}$ are coupled to the internal response through their respective dependence upon the rate at which the ablation gases are injected into the boundary layer. This system of equations does not have an analytic solution. Finite difference techniques have been successfully applied, but the numerical procedures are highly complex and detailed. Furthermore, a number of simplifying assumptions and a degree of empiricism must be introduced to make the problem, as outlined above, tractable.

It is the purpose of this paper to present a comprehensive and systematic review of laboratory experiments conducted in arc-jet wind tunnel test facilities which are directed toward isolating and quantitatively evaluating, on a macro-scopic scale:

- The surface heat shielding terms appearing in equation (2).
- The rate at which material recedes \dot{x}_{0} (eq. (3)).
- The degree of internal temperature rise as described by equation

Emphasis is placed upon determining the dependence of these phenomena upon the environmental parameters of pressure, enthalpy, and stream chemical composition. The results are intended to furnish a check on the assumptions underlying the computer programs used for design of heat shields. A variety of polymeric composites will be considered. These include:

1. Teflon - a long chain polymer characterized by an unzippering process ($\rho = 120 \text{ lb/ft}^3$).

2. Phenolic-nylon formulation of equal parts by weight which degrades to form a high temperature char layer ($\rho = 35$)1b/ft³).

3. Avcoat epoxy novolac resin in a glass honeycomb that decomposes to form a silica-containing char (ρ = 31 lb/ft³).

4. General Electric silicone elastomer which leaves a siliceous debris layer ($\rho = 37 \text{ lb/ft}^3$).

In order to judge the overall applicability and value of the experiments in terms of present and planned NASA missions, the first section of the paper will deal with the entry heating environments. Missions considered will range in severity from manned entry into the earth's atmosphere from earth orbit to the unmanned entry of an instrumented probe into the atmosphere of Venus. In addition to the stagnation region radiative and convective heating levels, the thermodynamic state of the vehicle boundary layer as characterized by the total enthalpy, chemical composition and pressure will also be presented and then compared to the current state-of-the-art simulation capability of arc-jet test facilities.

Having demonstrated the influence of mission constraints upon the imposed heating terms, which appear in equation 2, the paper will consider the various heating terms which arise from the interaction of the ablator and environment. Treated first are the identification of the chemical species and the blockage of convective heating. The work of Pope and Parker (ref. 1) is discussed. They utilized a time of flight mass spectrometer to identify the predominant chemical compounds in the boundary layer which occur when Teflon is ablated in both nitrogen and air streams. Next the influence of stream chemical composition upon the heat transfer to the Teflon surface is described. Here the work of Vojvodich and Pope (ref. 2) and some new data obtained by Pope at extremely high enthalpies is described. For a predominantly convective heating environment it is shown that as much as 85 percent of the imposed heating may be blocked by the Teflon vapors. Next, attention is focused on the reradiation capabilities of high temperature charring composites. Data, as obtained in phase I and II of the NASA-SRI Round Robin Ablation Program (ref. 3 and 4)--for the materials 2-4 listed on page 2 is presented. The results indicate that a sizable fraction of the heating may be dissipated by this very important mechanism. The effect of mode of heating (radiative vs. convective) is also discussed.

The surface position boundary condition (eq. (3)) is now considered. The rate of material removal has importance not only in terms of the heat protection problem, but also as it effects shape change and the associated aerodynamic characteristics of the entry vehicle. This latter consideration is of prime importance when the heat shield comprises a sizable fraction of the total vehicle weight. The surface recession data is presented as the ratio of surface mass loss rate $(p\dot{x})$ to the flow rate of oxygen reaching the surface $(pu)_{\text{oxy}}$ plotted as a function of surface temperature. This ratio is shown to be virtually independent of temperature for the phenolic nylon

char which is predominantly carbon. This evidence indicates that the rate limiting step in the removal process is the diffusion of oxygen to the surface. The results are found to agree favorably with both existing data (ref. 5 and 6) and the theory of Scala (ref. 7). In contrast to this finding, the data obtained with the epoxy resin and elastomeric composites show a marked dependence upon surface temperature. The results for these two

materials is replotted in the standard Arrhenius format ($\log x \log \frac{1}{T}$) and the rate constants and activation energies are derived and compared. Results are included for both stagnation region (ref. 8) and flat plate (ref. 9) experiments of the epoxy resin and the data are found to be relatively insensitive to test geometry and pressure level until severe levels of shear are encountered. The role of silica reactions in char removal is reviewed and discussed.

The internal processes are now considered. The fuclude char thickness dependence on environmental parameters and determination of pyrolysis gas enthalpy. The char thickness measurements for phenolic nylon are compared to those obtained for the elastomeric and epoxy resin composites. The results are also compared to the predictions based on a theoretical model developed in reference 10 which assumes quasi-steady state ablation in an environment where chemical removal predominates. Good agreement is demonstrated between experiment and theory at moderate pressure levels (p < 1.0atm). The enthalpy rise of the primary decomposition products of phenolic-nylon, as deduced from arc-imaging furnace measurements, are compared to theoretical calculations based on an assumption of complete thermochemical equilibrium. It is shown that for some conditions the gases may not be completely cracked as they pass through the high temperature char. The implications of this finding on heat shield performance is discussed.

The ultimate function and purpose of the varius heat shielding mechanisms is to limit the substructure of the spacecraft to a tolerable level of temperature during entry. To this end, comparisons of material systems are made on the basis of internal temperature measurements. Results from analytical programs are also included for selected environmental conditions.

As a guide to future areas of material research, calculations of heat shield requirements are presented for a manned return from Mars mission. These results have been generated in a parametric study conducted by Lockheed under a NASA contract described in reference 11. One of the purposes of the investigation was to determine the relative importance of various terms in the surface heat balance and accommodation of this heating by the internal capacity of the material—high density phenolic nylon. Emphasis was placed upon the influence of the uncertainties on the overall heat shielding requirements.

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